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Published in:
Journal of Materials Chemistry C

DOI:
[10.1039/c3tc32205j](https://doi.org/10.1039/c3tc32205j)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2014

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Salice, P., Ronchi, E., Iacchetti, A., Binda, M., Natali, D., Gomulya, W., Manca, M., Loi, M. A., Iurlo, M., Paolucci, F., Maggini, M., Pagani, G. A., Beverina, L., & Menna, E. (2014). A fulleropyrrolidine-squaraine blue dyad: synthesis and application as an organic light detector. *Journal of Materials Chemistry C*, 2(8), 1396-1399. <https://doi.org/10.1039/c3tc32205j>

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Supporting Information

A fulleropyrrolidine-squaraine blue dyad: synthesis and application as organic light detector

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1. Instruments, materials and methods

All the reagents and solvents were purchased from Sigma-Aldrich and were used as received if not otherwise specified. [60]Fullerene was purchased from Bucky USA and was used as received. Tetrabutylammonium hexafluorophosphate (TBAPF₆) was used, in the electrochemical experiments, as purchased from Sigma-Aldrich. Tetrabutylammonium hexafluoroarsenate (TBAAsF₆) was synthesized by metathesis reactions from tetrabutylammonium bromide with lithium hexafluoroarsenate and was recrystallized following the procedures reported in literature.¹ Dichloromethane (DCM) for CV measurements was prepared according to a reported procedure.² The procedure for the preparation of tetrahydrofuran (THF) is described in previous work.³ The solvents were then distilled into the electrochemical cell soon before performing the experiment.

Squaraine **2** was synthesized accordingly to a reported procedure.⁴ ¹H (500 MHz) and ¹³C (125.7 MHz) NMR spectra of a solution of the squaraine **2** in CD₂Cl₂ were recorded on a Bruker AMX-500 spectrometer.

Thin layer chromatography (TLC) and column chromatography were performed using a Polygram SiG/UV254 (TLC plates) and silica gel MN 60 (70–230 mesh) by Macherey-Nagel. ¹H (300.13 MHz) and ¹³C (75.03 MHz) NMR spectra of a solution of the dyad **1** in CDCl₃/CS₂ 4:1 were recorded on a Bruker Avance 300 (AV 300) spectrometer. ATR-IR spectra were collected on a Perkin Elmer Spectrum 100 FT-IR spectrophotometer equipped with an attenuated total reflection module (diamond). Spectra were measured at a resolution of 4 cm⁻¹. Absorption spectra in air-equilibrated solvents were registered with a Varian Cary 5000 spectrophotometer, at room temperature, between 280 and 800 nm, data interval = 0.5 nm, scan rate = 300 nm min⁻¹, SBW = 2 nm.

The dyad **1** mass fingerprints of selected spots were analyzed using a 4800 MALDI-TOF/TOF Plus Analyzer (Applied Biosystems, Foster City, CA, USA). Mass spectrum was obtained in the reflectron/delayed extraction mode at an accelerating voltage of 5 kV and sum data from either 500 laser pulses. 1,8,9-Anthracenetriol was used as matrix substance for MALDI-MS. The thermogravimetric analysis (TGA) of the dyad **1** was carried out with a Q5000IR TGA (TA Instruments) under air by heating at 10 °C/min rate till 200 °C.

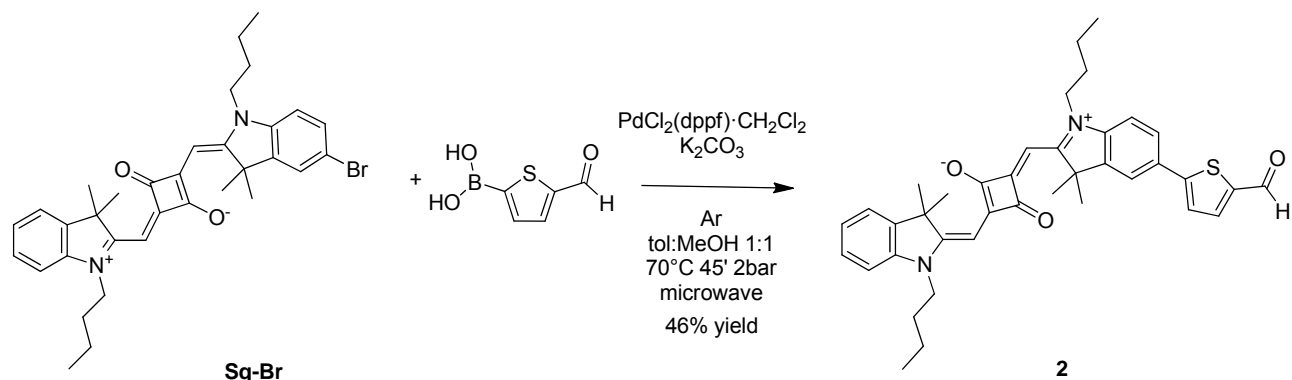
Optical measurements were performed on samples in solution contained in quartz cuvettes. The samples were excited at 380 nm by the second harmonic of a tunable mode-locked Ti:sapphire laser, characterized by 150 fs pulses and a repetition frequency of ~ 76 MHz.

The PL spectra were recorded with a monochromator coupled with a Si-CCD camera from Hamamatsu, and corrected for the spectral response of the set up. Time-resolved signals were detected with a Hamamatsu streak camera with a photocathode sensitive in the visible working in synchroscan mode. The time resolution is about 2 ps. All the measurements were carried out at room temperature.

Electrochemical measurements were performed in one-compartment airtight electrochemical cell with high-vacuum glass stopcocks fitted with Viton O-Ring in order to prevent contamination by grease. The connections to the high-vacuum line and to the Schlenk containing the solvent were obtained by spherical joints also fitted with Viton O-ring. The pressure measured in the electrochemical cell prior to performing the trap-to-trap distillation of the solvent was 3.0 × 10⁻⁵ mbar. The working electrode was a 125 μm diameter platinum wire (about 0.012 mm²) sealed in glass. The counter electrode consisted of a platinum spiral and the quasi-reference electrode was a silver spiral. The quasi-reference electrode drift was negligible for the

time required by single experiment. Both the counter and the reference electrode were separated from the working electrode by ~0.5 cm. Potentials were measured with the decamethylferrocene standard and were always referred to SCE. $E_{1/2}$ values correspond to $(E_{pc}+E_{pa})/2$ from CV. Decamethylferrocene was also used as an internal standard for checking the electrochemical reversibility of a redox couple. Voltammograms were recorded with an home-made potentiostat controlled by either an AMEL Model 568 function generator. Data acquisition was performed by a Nicolet Mod 3091 digital oscilloscope interfaced to a PC. Solid state electrochemical experiments were performed on ITO (Indium Tin Oxide) electrode. The dyad **1** was supported on ITO substrates by drop casting 100 μ L of 1.16 mg / mL dichloromethane solutions. The measurements are carry out in H₂O solution using as supporting electrolyte 0.05 M LiClO₄.

2. Synthesis and characterization of the squaraine 2.



Squaraine **2** was synthesized accordingly to a reported procedure.⁴ Briefly, squaraine **Sq-Br** (100 mg, 0.17 mmol) and finely ground anhydrous potassium carbonate (117.49 mg, 0.85 mmol) were added to a microwave tube. 5-Formylthiophen-2-ylboronic acid (79 mg, 0.51 mmol) and $\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (14 mg, 0.017 mmol) were added to the tube in glove box under argon atmosphere. Anhydrous toluene (2 mL) and anhydrous methanol (2 mL) were added to the reagents to give a blue suspension. The microwave tube was sealed under argon atmosphere. The reaction mixture was stirred in the dark at room temperature while setting up the microwave. The microwave reactor (CEM Discover) was set to: standard mode, $T = 70^\circ\text{C}$, Powermax = 60 W, pressuremax = 5 bar, stirring = high, cooling off, hold time = 30 min. The reaction mixture turned teal blue. Four batches were combined and the solvent was evaporated under reduced pressure to give a dark solid. The product was purified by column chromatography (elution from $\text{CHCl}_3:\text{EtOAc}$: 1:1 to $\text{CHCl}_3:\text{MeOH}$ 9:1). The first fraction collected (100 mg) was a 1:1 mixture of the product and the reagent **Sq-Br**, which was purified by a second column chromatography with the same eluent. The second fraction collected gave the pure product as metallic green needles after solvent evaporation (190 mg, 0.31 mmol, 46% yield).

$^1\text{H-NMR}$ (300 MHz, CD_2Cl_2 , δ): 9.91 (s, 1H), 7.81 (d, $J = 4.0$ Hz, 1H), 7.71 (dd, $J_1 = 8.2$ Hz, $J_2 = 1.7$ Hz), 7.68 (s, 1H), 7.47 (d, $J = 4.0$ Hz, 1H), 7.44 (d, $J = 7.1$ Hz, 1H), 7.39 (t, $J = 7.2$ Hz, 1H), 7.24 (t, $J = 7.4$ Hz, 1H), 7.13 (d, $J = 8.0$ Hz, 1H), 7.07 (d, $J = 8.3$ Hz, 1H), 6.11-6.05 (m, 2H), 1.90-1.75 (m, 18H), 1.57-1.50 (m, 5H), 1.05 (t, $J = 7.4$ Hz, 6H). $^{13}\text{C-NMR}$ (75 MHz, $\text{CS}_2:\text{CDCl}_3$, δ): 183.41, 154.82, 143.28, 143.19, 142.76, 138.58, 129.09, 128.74, 127.38, 125.14, 124.45, 123.13, 121.05, 110.91, 110.57, 88.28, 88.18, 50.50, 49.69, 44.67, 44.45, 30.56, 30.11, 29.95, 27.79, 27.40, 21.20, 14.53, 14.51. APPI-MS: m/z : 618 [M-].

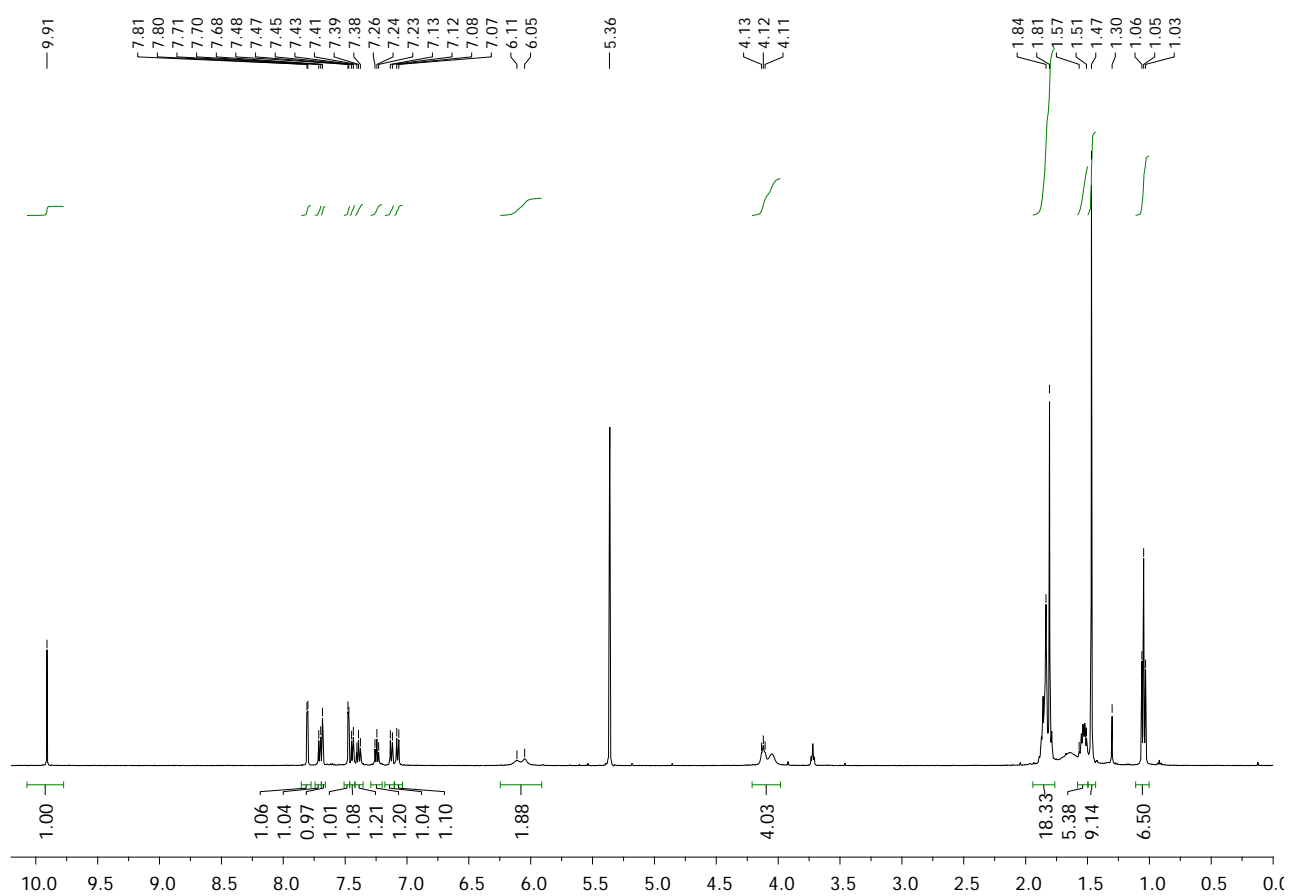


Figure S1. ¹H-NMR spectrum of squaraine 2 (300 MHz, CD₂Cl₂).

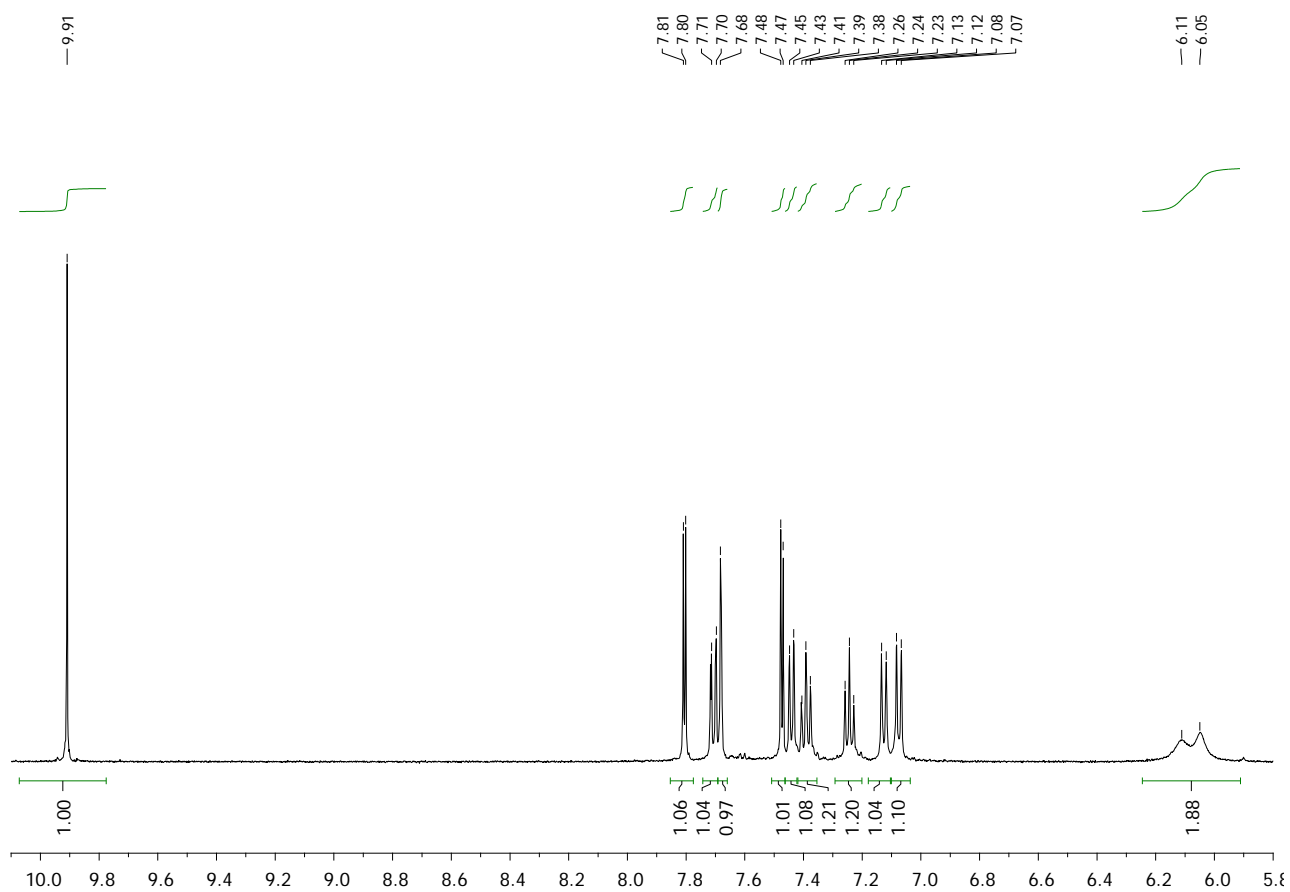


Figure S2. $^1\text{H-NMR}$ spectrum of squaraine **2** (500 MHz, CD_2Cl_2).

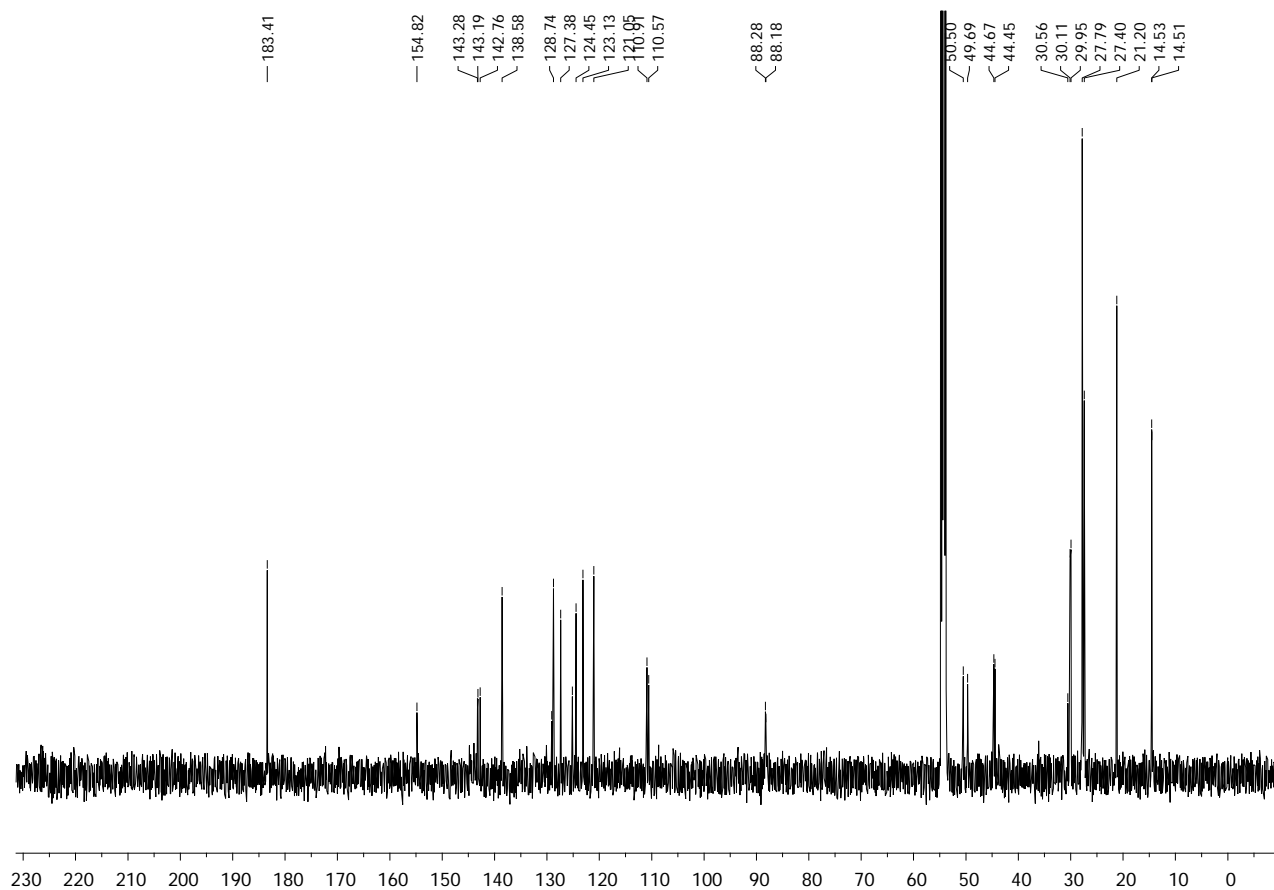


Figure S3. ^{13}C -NMR spectrum of squaraine **2** (125 MHz, CD_2Cl_2).

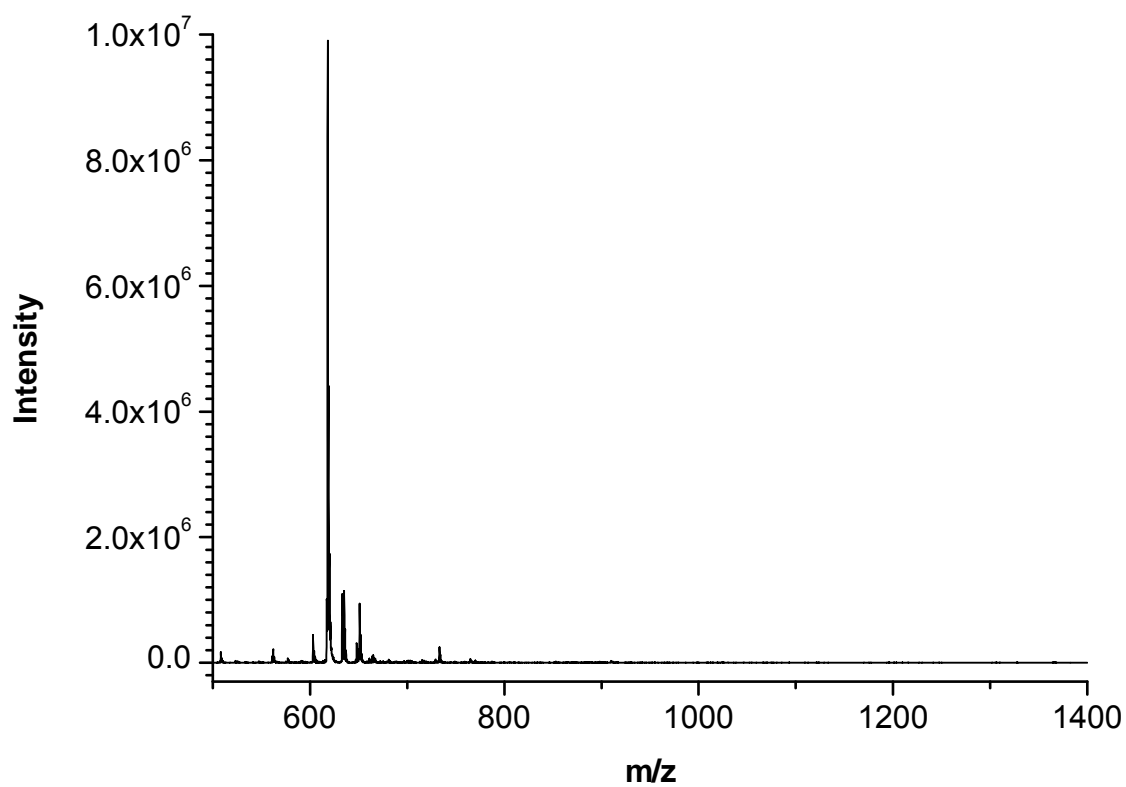


Figure S4. APPI-MS spectrum of the squaraine **2**.

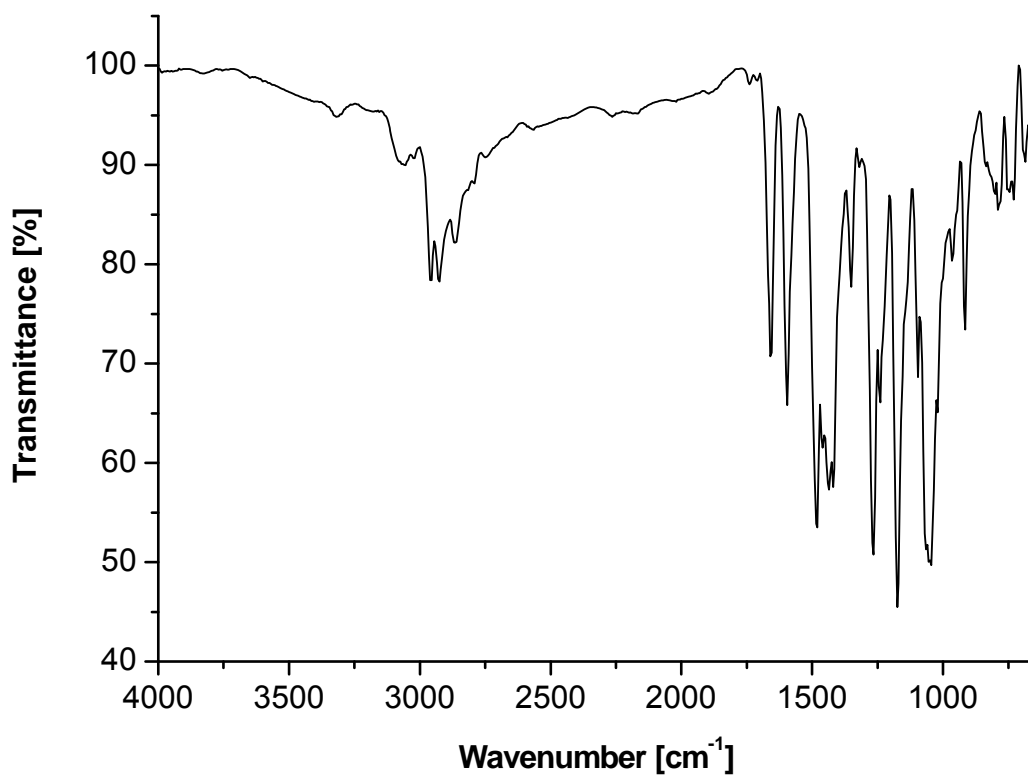
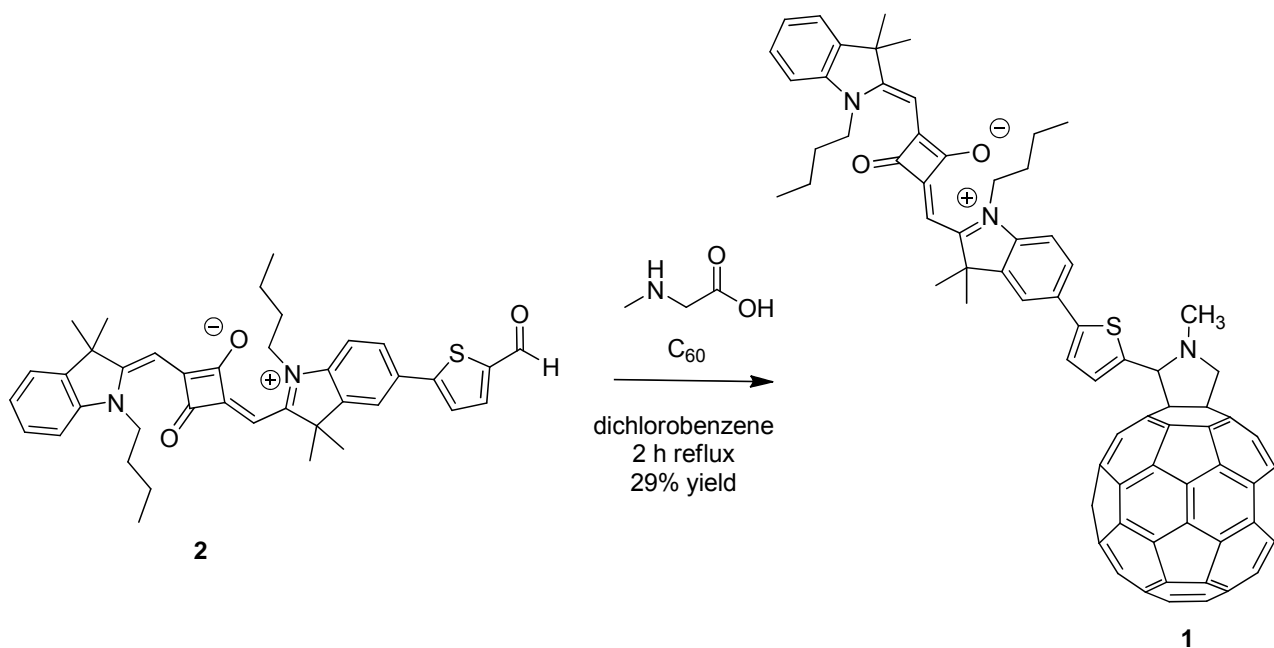


Figure S5. ATR-IR spectrum of the squaraine 2.

3. Synthesis and characterization of the dyad 1



The reaction was performed under nitrogen in the dark. A solution of the aldehyde **2** (23 mg, 0.037 mmol) in 1,2-dichlorobenzene (2 mL) was added to a refluxing solution of [60]fullerene (27 mg, 0.037 mmol) in 1,2-dichlorobenzene (5 mL). Finely ground sarcosine (5 mg, 0.056 mmol) was then added portionwise. The reaction mixture was refluxed for 2 hours and then the solvent was removed under reduced pressure. The bluish residue was washed with methanol:toluene 9:1 (7 x 5 mL) to remove the non-fullerene byproducts and was purified by column chromatography on silica gel (elution gradient from chloroform to chloroform:methanol 96:4, $R_f(2) = 0.8$, $R_f(1) = 0.74$). The desired product was obtained as a purple metallic solid (15 mg, 0.011 mmol, 29% yield).

^1H NMR (300 MHz, $\text{CS}_2:\text{CDCl}_3$, δ): 7.61-7.58 (m, 2H), 7.46-7.43 (m, 4H), 7.30 (d, $J = 3.7$ Hz, 1H), 7.28-7.20 (m, 2H), 7.14 (d, $J = 3.7$ Hz, 1H), 7.06 (t, $J = 7.4$ Hz, 1H), 6.91-6.84 (m, 1H), 5.86-5.84 (m, 2H), 5.19 (s, 1H), 4.96 (d, $J = 9.5$ Hz, 1H), 4.23 (d, $J = 9.6$ Hz, 1H), 4.11 (dd, $J_1 = 3.3$, $J_2 = 5.8$, 6H), 2.92 (s, 3H), 1.74-1.70 (m, 12H), 1.50-1.20 (m, 33H), 1.00 (t, $J = 7.26$ Hz, 6H). ^{13}C -NMR (75 MHz, $\text{CS}_2:\text{CDCl}_3$, δ): 171.41, 169.95, 168.26, 157.33, 155.29, 154.59, 154.48, 148.85, 148.36, 147.91, 147.88, 147.85, 147.80, 147.78, 147.74, 147.69, 147.65, 147.50, 147.32, 147.22, 147.17, 147.02, 146.97, 146.94, 146.90, 146.86, 146.84, 146.81, 146.73, 146.27, 146.22, 145.92, 144.73, 144.66, 144.58, 144.29, 144.18, 143.91, 143.84, 143.76, 143.73, 143.69, 143.63, 143.54, 143.51, 143.49, 143.25, 143.20, 141.80, 141.58, 141.36, 138.70, 138.25, 137.42, 137.17, 134.16, 132.09, 131.48, 130.61, 130.32, 129.38, 127.15, 125.53, 123.92, 123.53, 121.33, 110.91, 88.98, 80.97, 79.31, 78.89, 78.47, 71.61, 70.22, 69.25, 50.84, 45.06, 41.99, 40.59, 32.32, 31.69, 30.98, 30.85, 28.85, 28.82, 28.66, 25.81, 25.10, 22.39, 16.04, 15.80, 12.92. APPI-MS: m/z : 1366 [M $^-$]; MALDI TOF/TOF: m/z calcd for $\text{C}_{101}\text{H}_{47}\text{N}_3\text{O}_2\text{S}_3$: 1365.339; found: 1365.401.

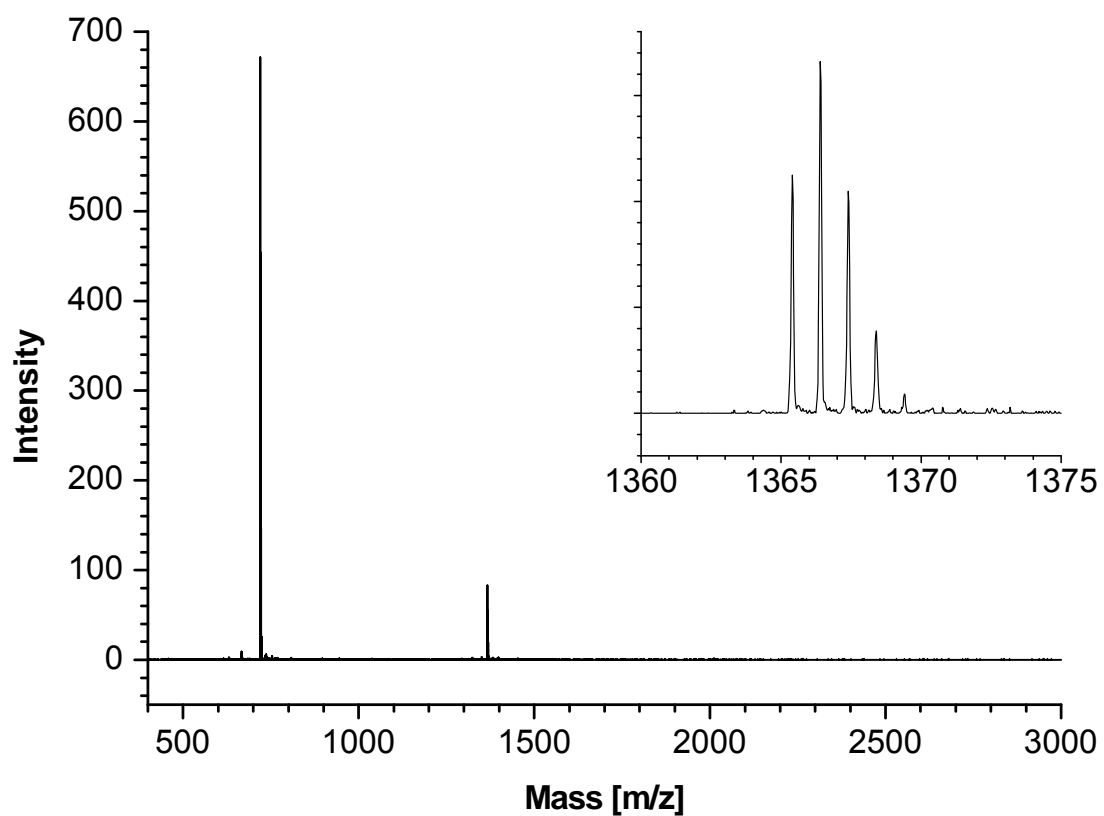


Figure S6. MALDI TOF/TOF mass spectra of the dyad **1** using 1,8,9-anthracenetriol as matrix (5 kV, 500 laser pulses).

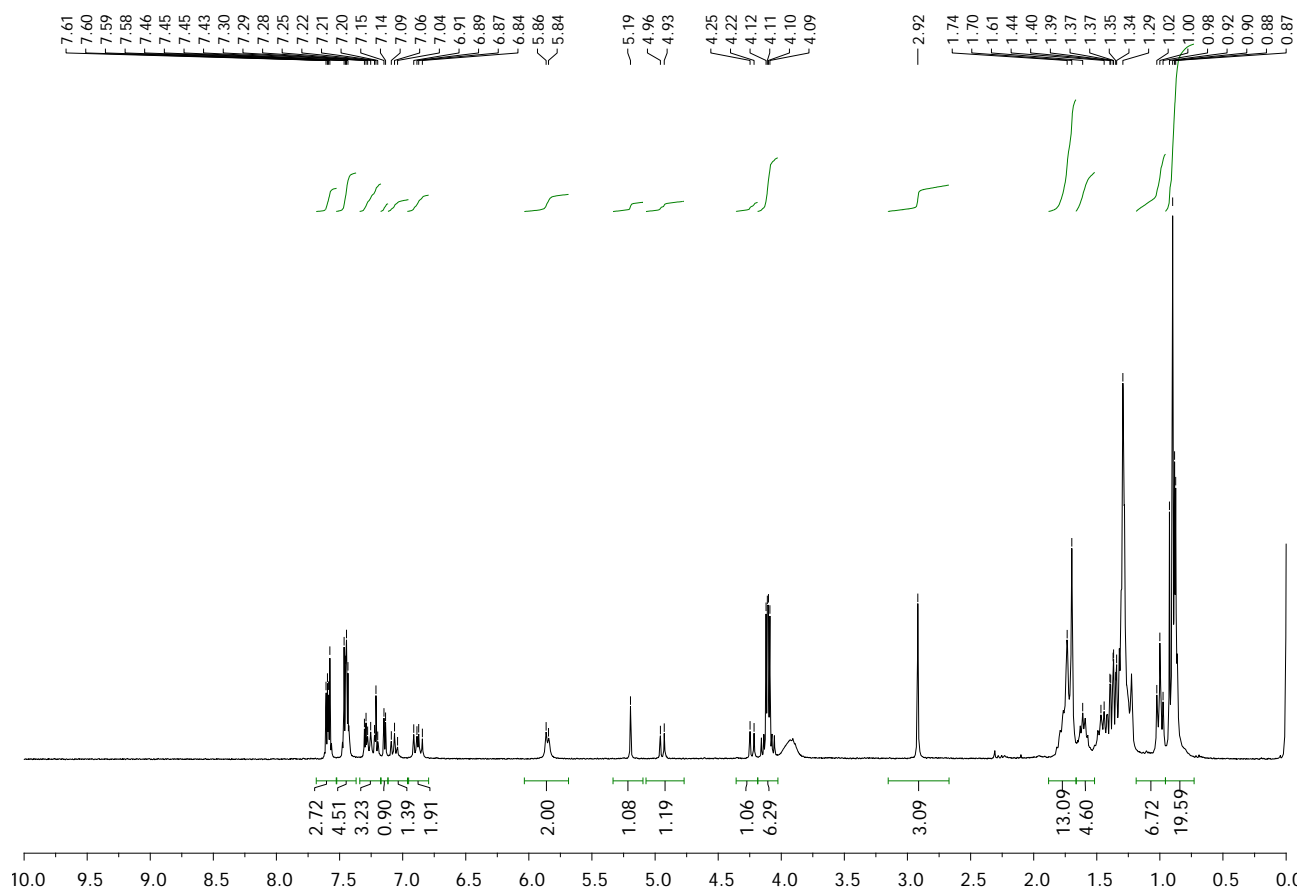


Figure S7. $^1\text{H-NMR}$ spectrum of the dyad **1** (300 MHz, $\text{CDCl}_3/\text{CS}_2$ 4:1).

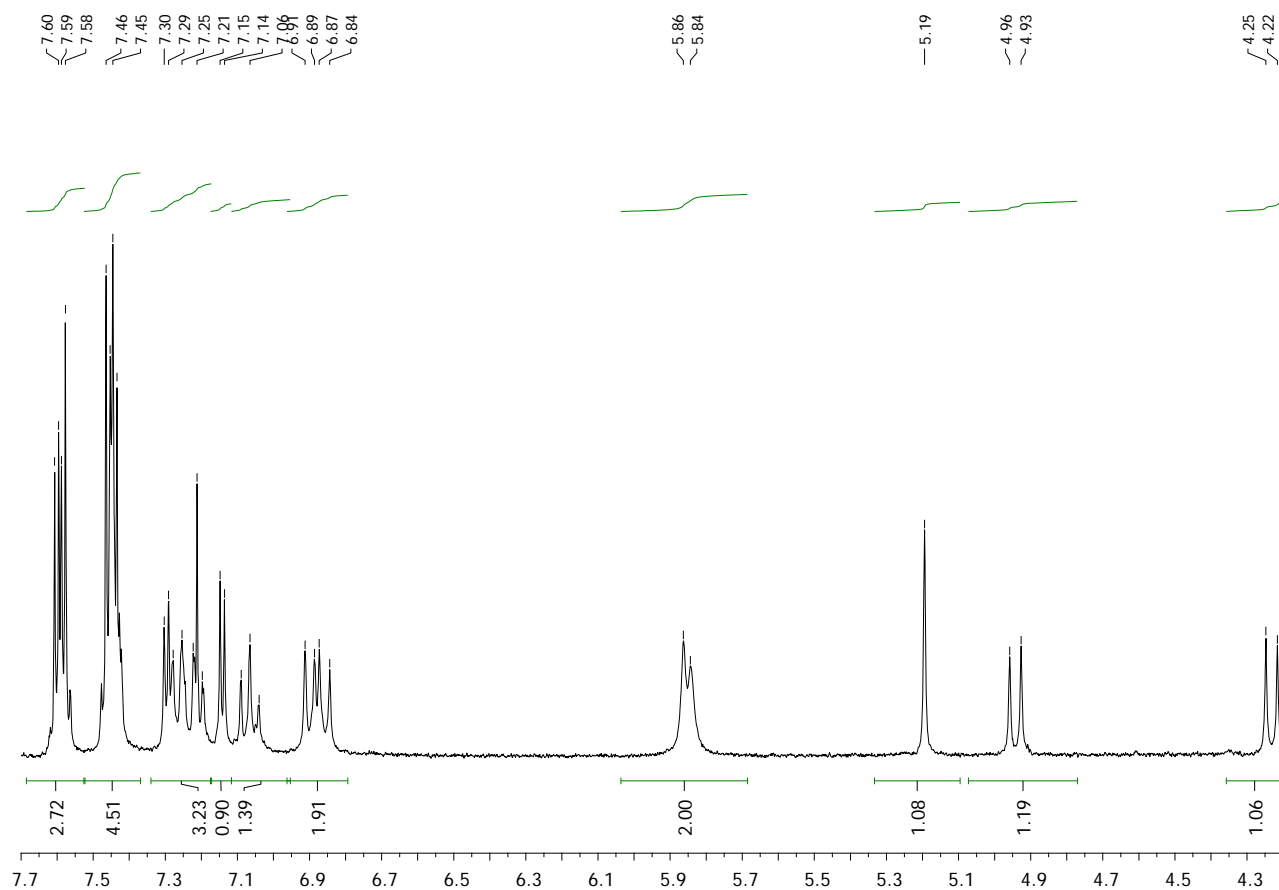


Figure S8. The region between 4.2 and 7.7 ppm of the ¹H-NMR spectrum of 1 (300 MHz, CDCl₃/CS₂ 4:1) highlights the presence of the 3 protons of the pyrrolidine rings at 4.23, 4.94 and 5.19 ppm. The signals between 5.86 and 5.84 ppm have been assigned to the methylene protons of the squaraine backbone. The signals at 7.30 and 7.14 ppm have been assigned to the thiophene proton. All the other signals between 7.7 and 6.8 ppm are representative of the aromatic protons of the two benzothiazole groups.

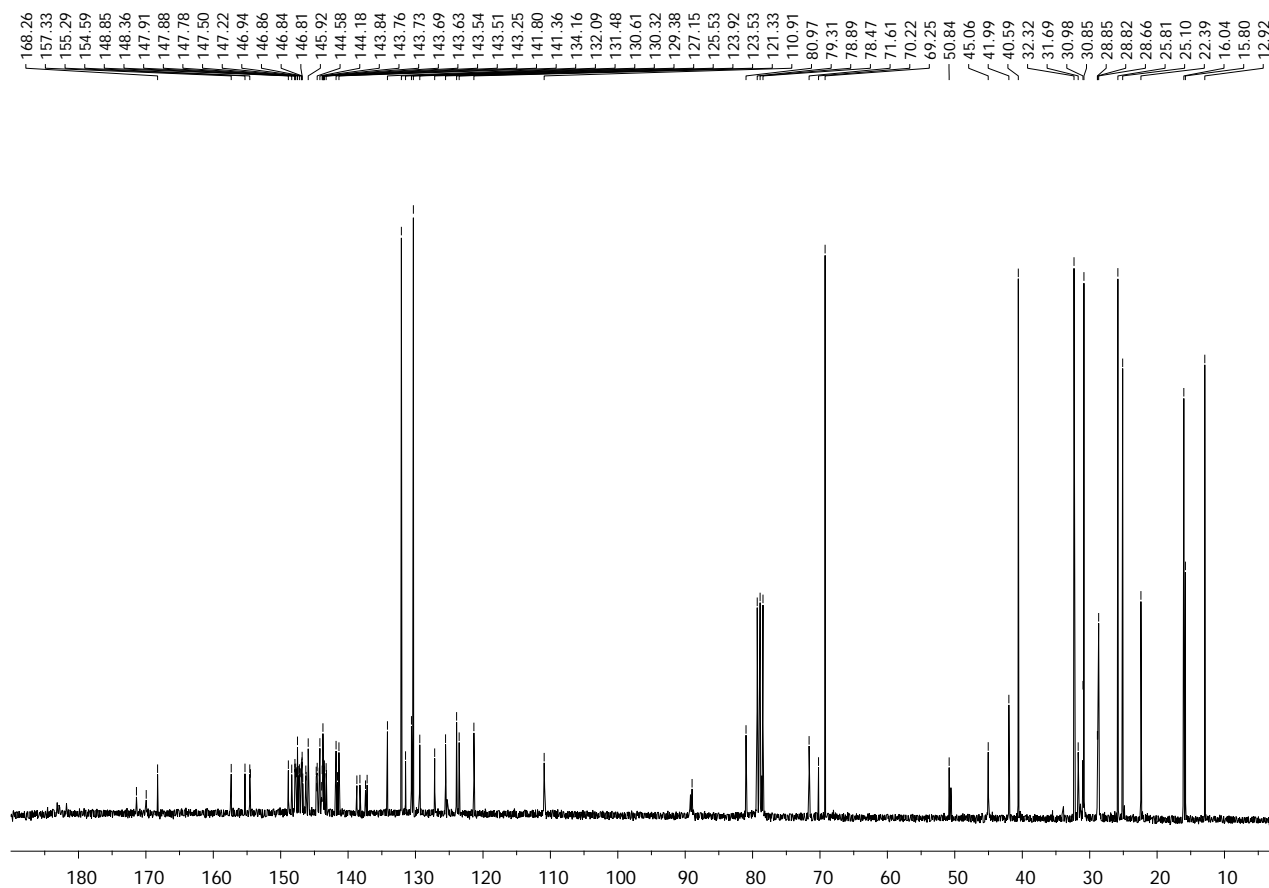


Figure S9. ^{13}C -NMR spectrum of **1** (75 MHz, $\text{CDCl}_3/\text{CS}_2$ 4:1).

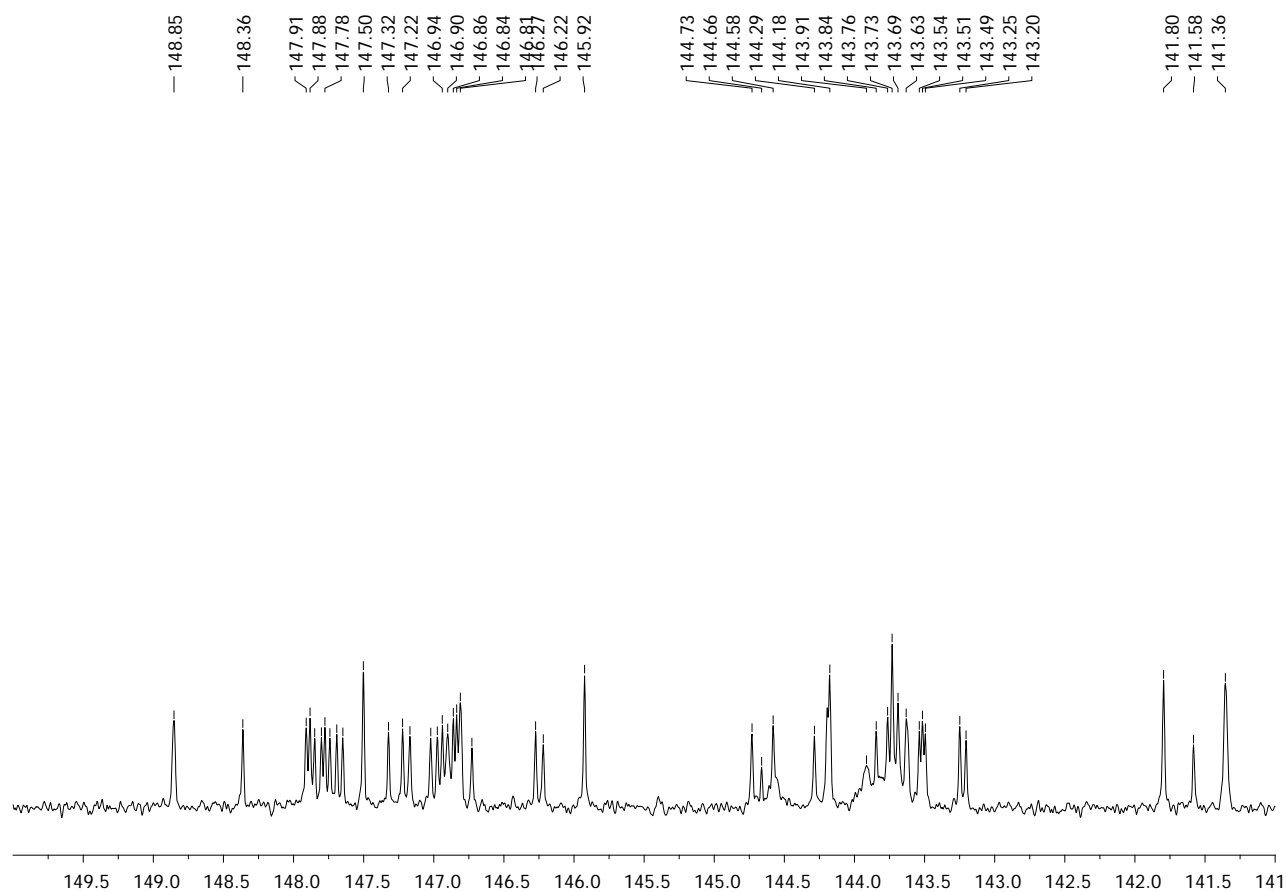


Figure S10. ^{13}C -NMR spectrum of **1** (75 MHz, $\text{CDCl}_3/\text{CS}_2$ 4:1).

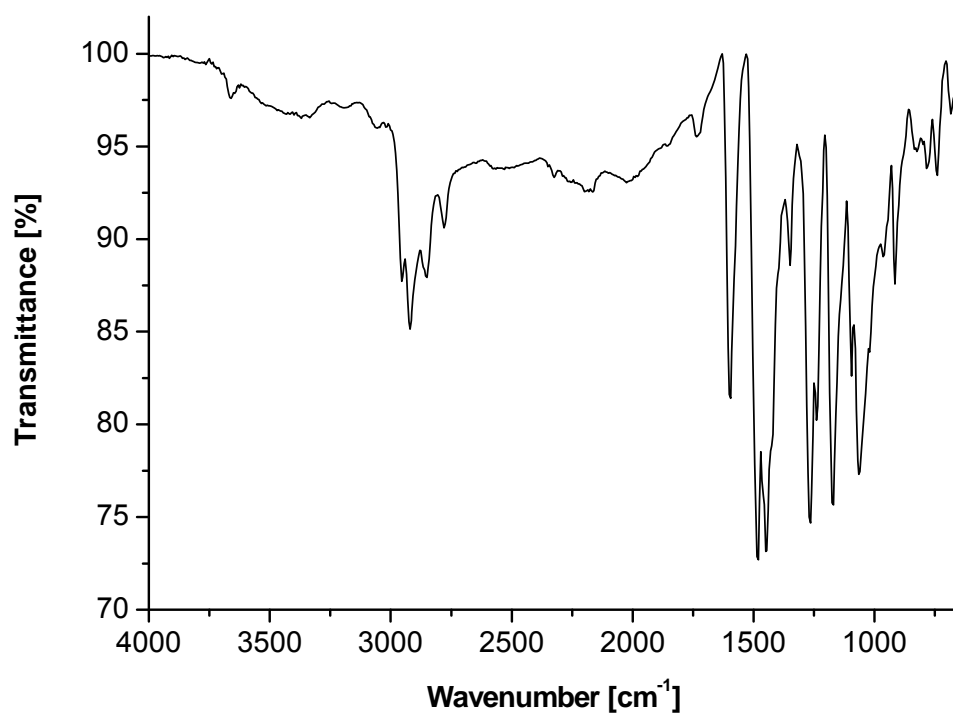


Figure S11. ATR-IR spectrum of the dyad 1.

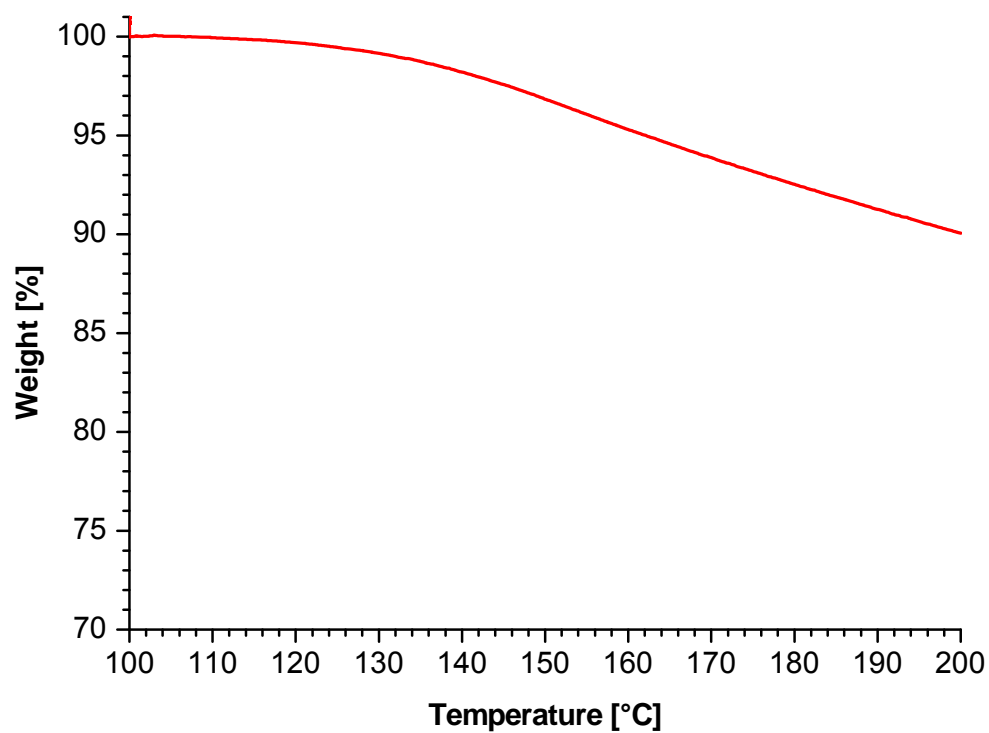


Figure S12. Thermogravimetric analysis of the dyad **1** under nitrogen atmosphere (heating rate: 10 °C/min). The weight loss at 130 °C is 1% and demonstrates that the dyad has an excellent thermal stability.

4. Optical properties and PL measurements

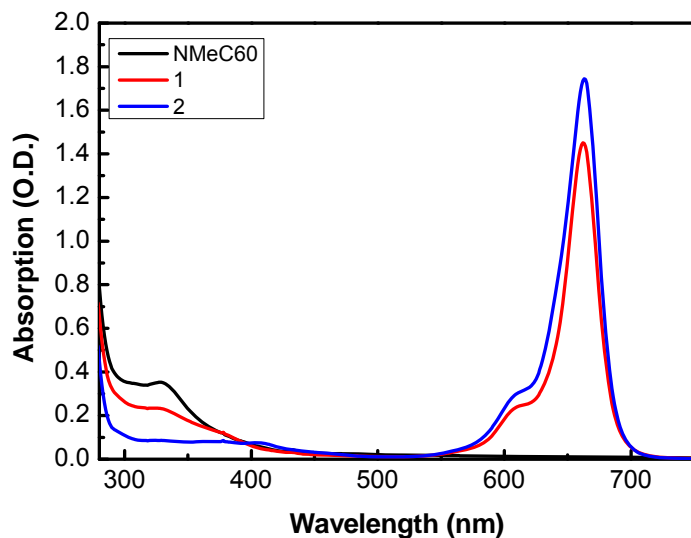


Figure S13. UV-vis absorption spectra of the dyad **1** (red line), the squaraine **2** (blue line) and the *N*-methylpyrrolidine derivative of [60]fullerene (NMeC60,⁵ black line) in toluene.

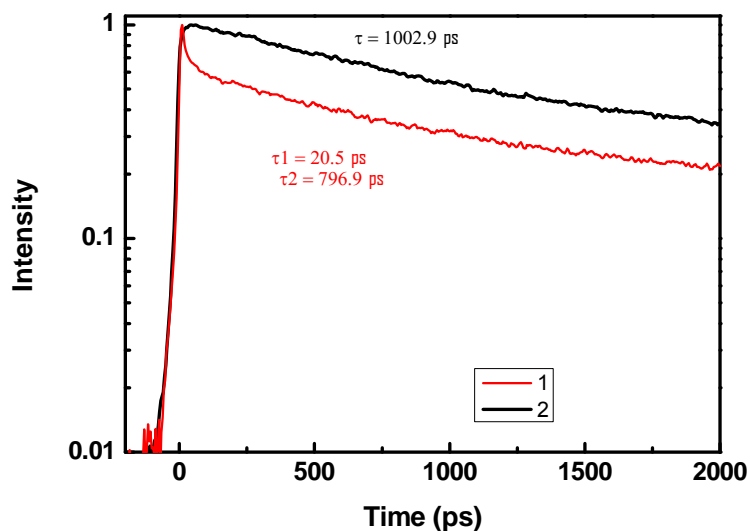


Figure S14. Time-domain intensity decay of the emission at 678 nm after excitation at 380 nm of solutions of the dyad **1** (red line) and of the squaraine **2** (black line) in toluene. The data reported were obtained by fitting the decay curves with exponential functions.

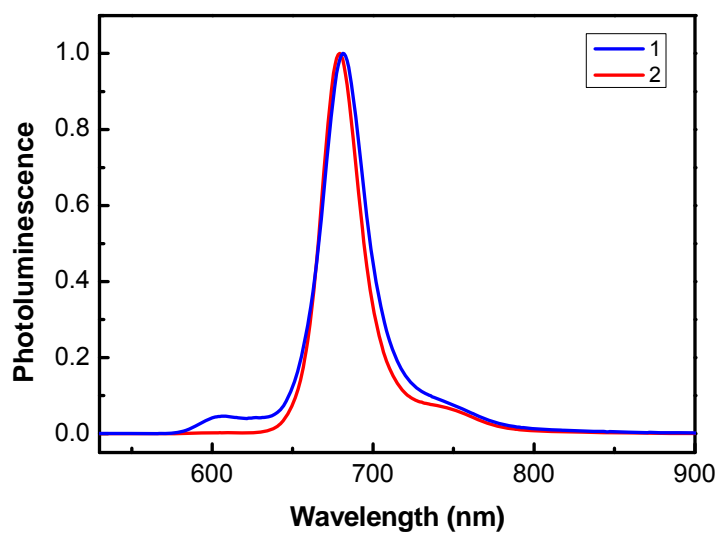


Figure S15. Normalized fluorescence emission spectra of the dyad **1** (red line) and of the squaraine **2** (blue line) in toluene after excitation at 380 nm.

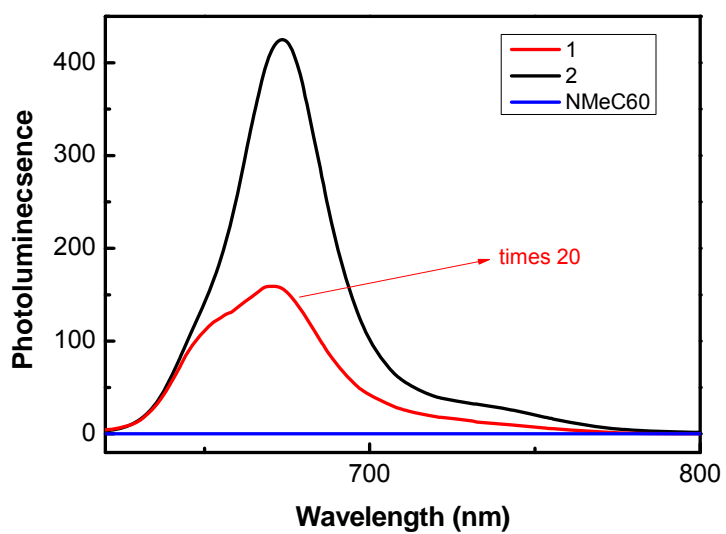


Figure S16. Photoluminescence spectra of the dyad **1** (red line), of the squaraine **2** (black line) and of the *N*-methylpyrrolidine derivative of [60]fullerene (NMeC60, blue line) in toluene after excitation at 600 nm.

5. Electrochemical characterization

Figure S17 shows the CV curve for a 0.1 mM DCM solution of dyad. Two oxidations corresponding to A and B peaks, due to the electronrich moieties of the squaraine backbone,⁶ at half-wave potentials $E_{1/2}$ of +0.44 and +0.93 V respectively, and a reversible one-electron reduction at an $E_{1/2}$ of -1.30 V (IV peak)⁷ were observed. Peak I relate to aspecific adsorption on electrode surface, infact after the first scan there is a disappearance of this peak (not shown). The three remaining reductions (II, III and V) were attributed to redox processes involving the fullerene moiety. The electrochemistry behaviour of dyad was also explored in THF solution (Figure S18). AsF₆⁻ anion is known for its high oxidation resistance and low nucleophilicity, the formed cations are stabilized using the TBAAsF₆. In anodic region a slight shift to lower potentials positive compared to DCM was noted.³ Instead the reduction processes are shifted to more negative potential. Also in THF an inappreciable adsorption is occurs. The high degree of chemical reversibility proves that the radical ions and the di-cations are stable on the voltammetric timescale.

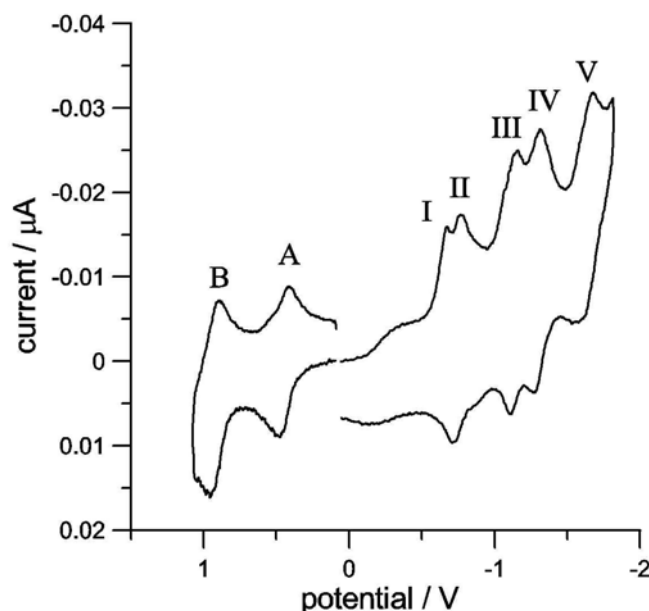


Figure S17. Cyclic voltammetric curves (two single scans) of dyad **1** 0.1 mM in a 0.05 M TBAPF₆/DCM solution. Working electrode Pt disk 125 μm (diameter); reference electrode SCE; scan rate= 1 V/s, T = 298 K.

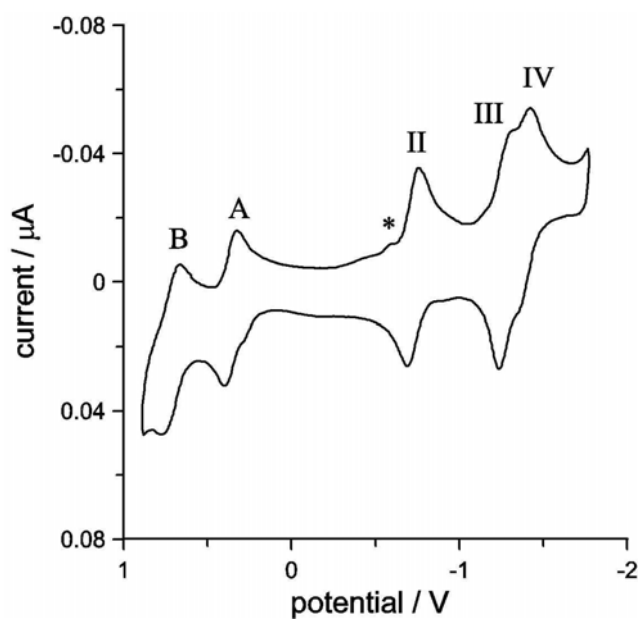


Figure S18. Cyclic voltammetric curves of dyad **1** 0.3 mM in a 0.05 M TBAAsF₆/THF solution. The small peaks (shoulders) close to the reduction (labeled by asterisks) are due to the presence of adsorption. Working electrode Pt disk 125 µm (diameter); reference electrode SCE; scan rate= 1 V/s, T = 298 K.

Table S1. $E_{1/2}$ values (V vs. SCE) of redox couples of dyad **1** detected by CV experiments (sweep rate = 1 V s⁻¹, at 298 K).^a

Solvent/supporting electrolyte	I	II	III	IV	V	VI	A	B
DCM/TBAH ^b	-0.67 ^c	-0.74	-1.13	-1.30	-1.64		+0.44	+0.93
THF/TBAAsF ₆ ^d		-0.72	-1.30	-1.39	-1.90 ^e	-2.36 ^e	+0.36	+0.72

^a Working electrode: Pt. ^b 0.1 mM. ^c the potential referred to adsorption peak. ^d 0.3 mM. ^e view Fig. S19 in Supporting Information

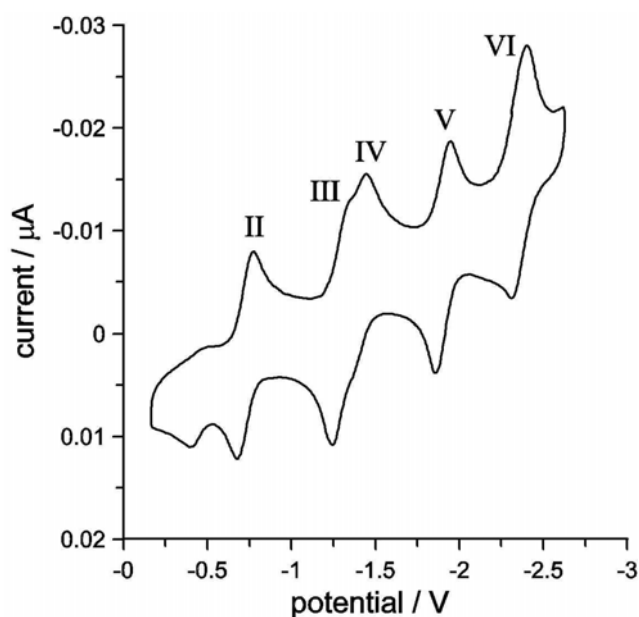


Figure S19. Cyclic voltammetric curves of dyad **1** 0.3 mM in a 0.05 M TBAAsF₆/THF solution. Working electrode Pt disk 125 μm (diameter); reference electrode SCE; scan rate= 1 V/s, T = 298 K.

Table S2. Squaraine-centered redox processes in dyad and squaraine alone versus Saturated Calomel Electrode (SCE) for solution in DCM.

Compound	I	II	A	B
1	-1.30	N.A.	+0.44	+0.93
2	-1.27	-1.76	+0.47	+0.93

Data were recorded with Tetrabutylammonium hexafluorophosphate as the supporting electrolyte.

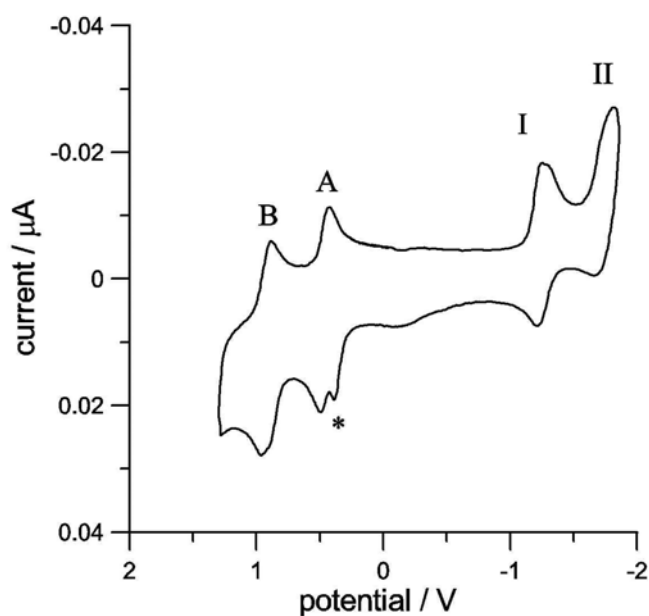


Figure S20. Cyclic voltammetric curves of squaraine **2** in a 0.05 M TBAPF₆/DCM solution. Working electrode Pt disk 125 μm (diameter); reference electrode SCE; scan rate= 1 V/s, T = 298 K.

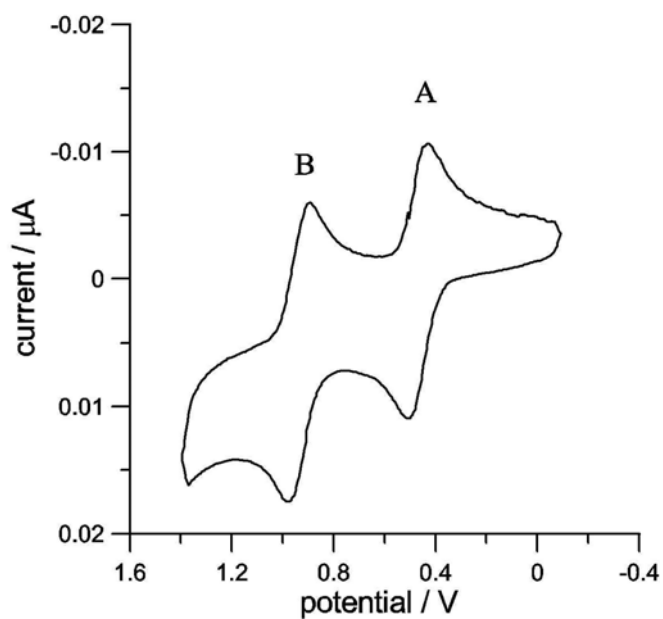


Figure S21. Cyclic voltammetric curves of squaraine **2** in a 0.05 M TBAPF₆/DCM solution. Working electrode Pt disk 125 μm (diameter); reference electrode SCE; scan rate= 1 V/s, T = 298 K.

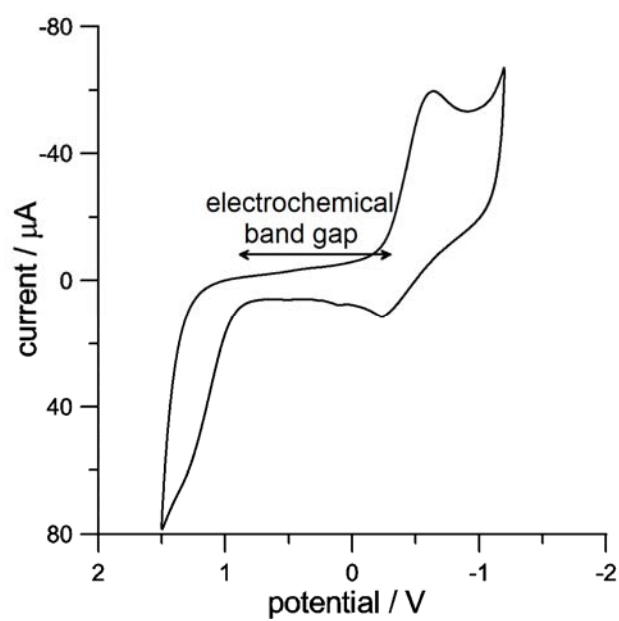


Figure S22. Cyclic voltammetric curves of drop cast dyad **1** in 0.05 M LiClO₄/H₂O solution. Working electrode ITO 6mm (diameter); reference electrode SCE; scan rate= 0.1 V/s, T = 298 K.

6. Photodiode fabrication and testing

ITO substrates (XinYan Technology Ltd) were cleaned by scrubbing them with lens cleaning paper imbued with chloroform, acetone and isopropanol and then treated with oxygen plasma. PEDOT:PSS (Clevios P VP Al 4083) was spin-coated on top (2000 rpm for 30 s) and annealed for 15 min in glove box to yield a 40nm thick film. The dyad **1** was dissolved in chloroform (10 mg/mL), stirred overnight and deposited by spin-coating (100 rpm for 60 s followed by 1000 rpm for 60 s) in glovebox. An aluminum cathode was deposited by thermal evaporation defining a device area of 1 mm².

All measurements were performed in vacuum (below 10⁻⁶ mbar). Devices were illuminated with a set of LEDs whose emitted light intensity was measured with a Si pin photodiode (Siemens BPX-65). DC electrical measurements were performed by means of Agilent B1500A, whereas transient current measurements were performed by means of a home-made low-noise transimpedance amplifier.

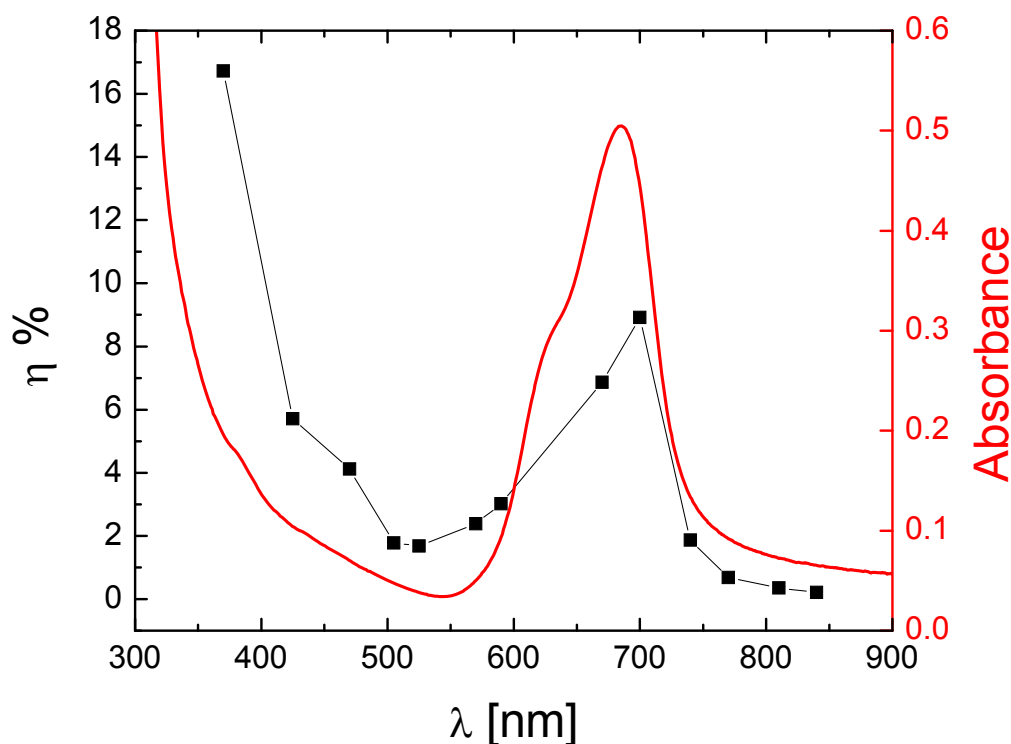


Figure S23. EQE when biasing the device in reverse ($V_{Al}-V_{ITO} = 1$ V), illuminating the device with 500 μ s long light pulses (light intensity about 10 mW/cm²). In red the film solid state absorbance.

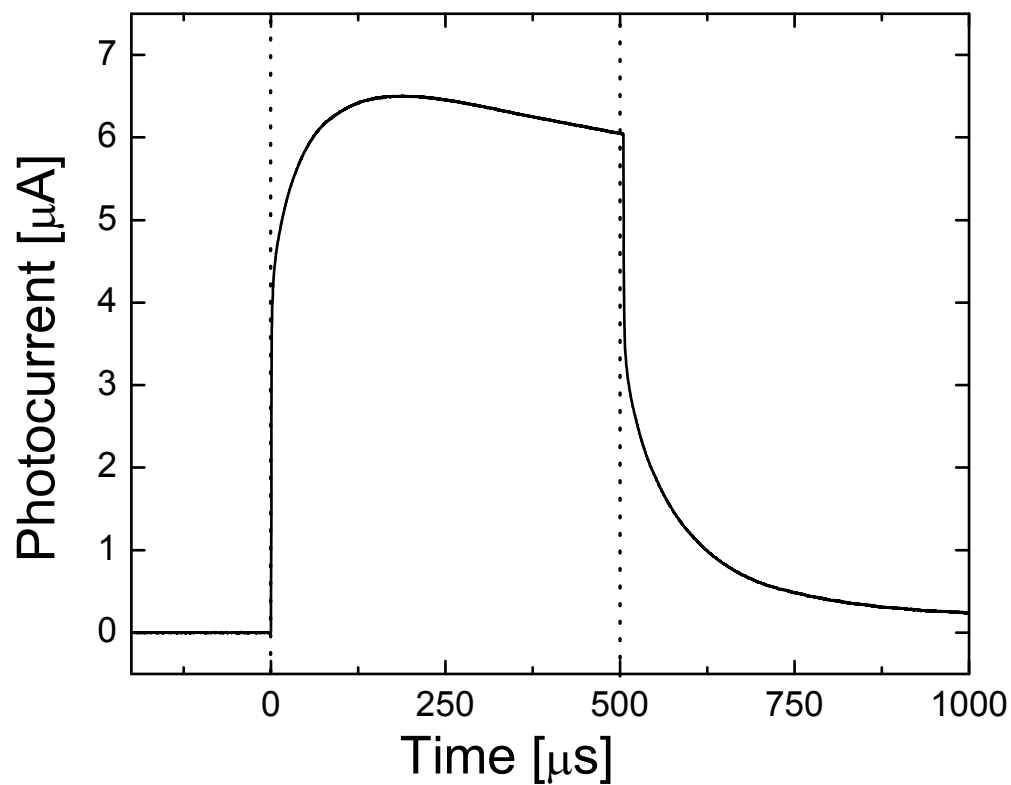


Figure S24. Photocurrent as a function of time upon 500 μs light pulse (indicated by dotted lines) at 670 nm. As far as the photocurrent fall-off, it is possible to appreciate a fast component followed by a slow tail (likely due to charge detrapping).

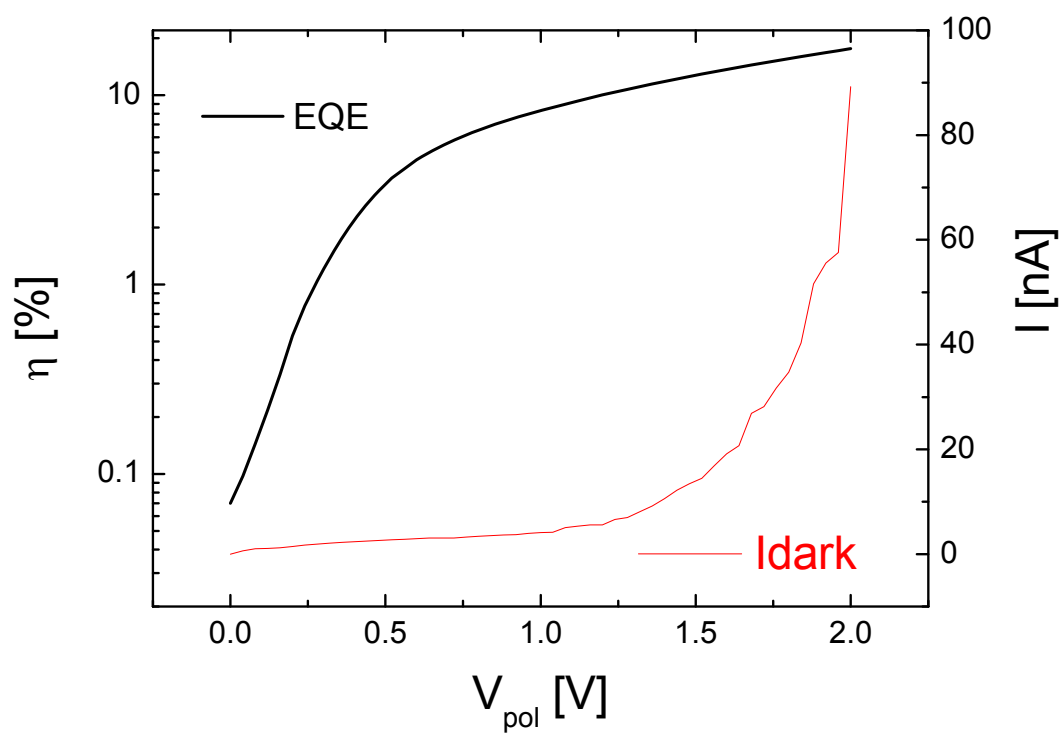


Figure S25. Dependence of the EQE on the applied voltage for $\lambda = 670$ nm (incident power density 4.96 mW/cm²). At 0 V applied, the EQE is fairly low (below 0.1%), but at it reaches 20% at 2 V. Higher voltages were not applied because of the fast rising of I_{dark} for voltage bias in excess of 1.7 V.

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